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(54) **Dispersion-strengthened  
copper alloys**

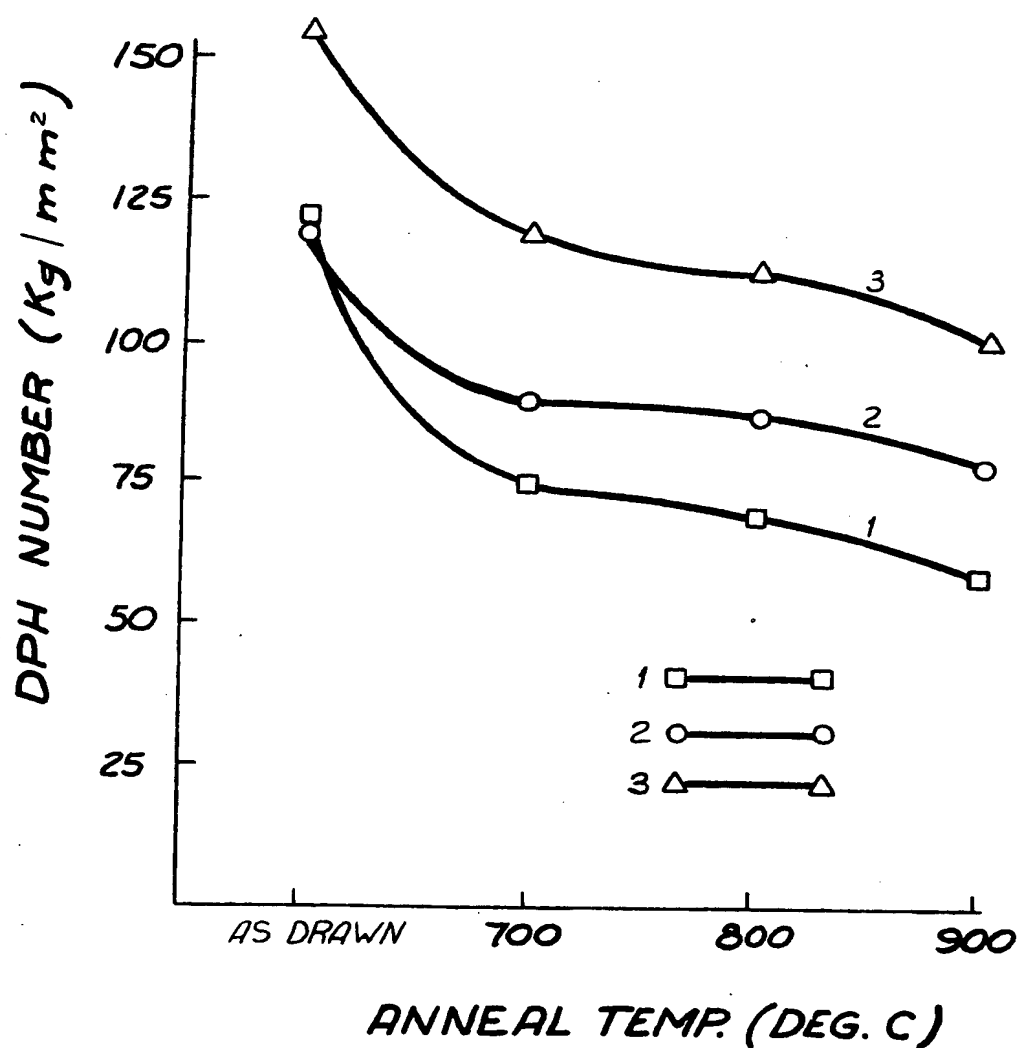
(57) Dispersion strengthened copper alloy products comprise a sintered matrix of copper metal particles having uniformly dispersed therein smaller size particles of aluminum oxide. These materials exhibit mechanical properties of tensile

strength, yield strength, hardness and ductility intermediate between copper-chromium alloys and internally oxidized copper alloys dispersion strengthened with aluminum oxide particles, and further exclude any significant solution alloy content. Preferred dispersion alloy products contain 0.1 weight percent up to 1.2 weight percent aluminum oxide.

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Fig. 1

DIAMOND PYRAMID HARDNESS  
vs  
ANNEAL TEMPERATURE

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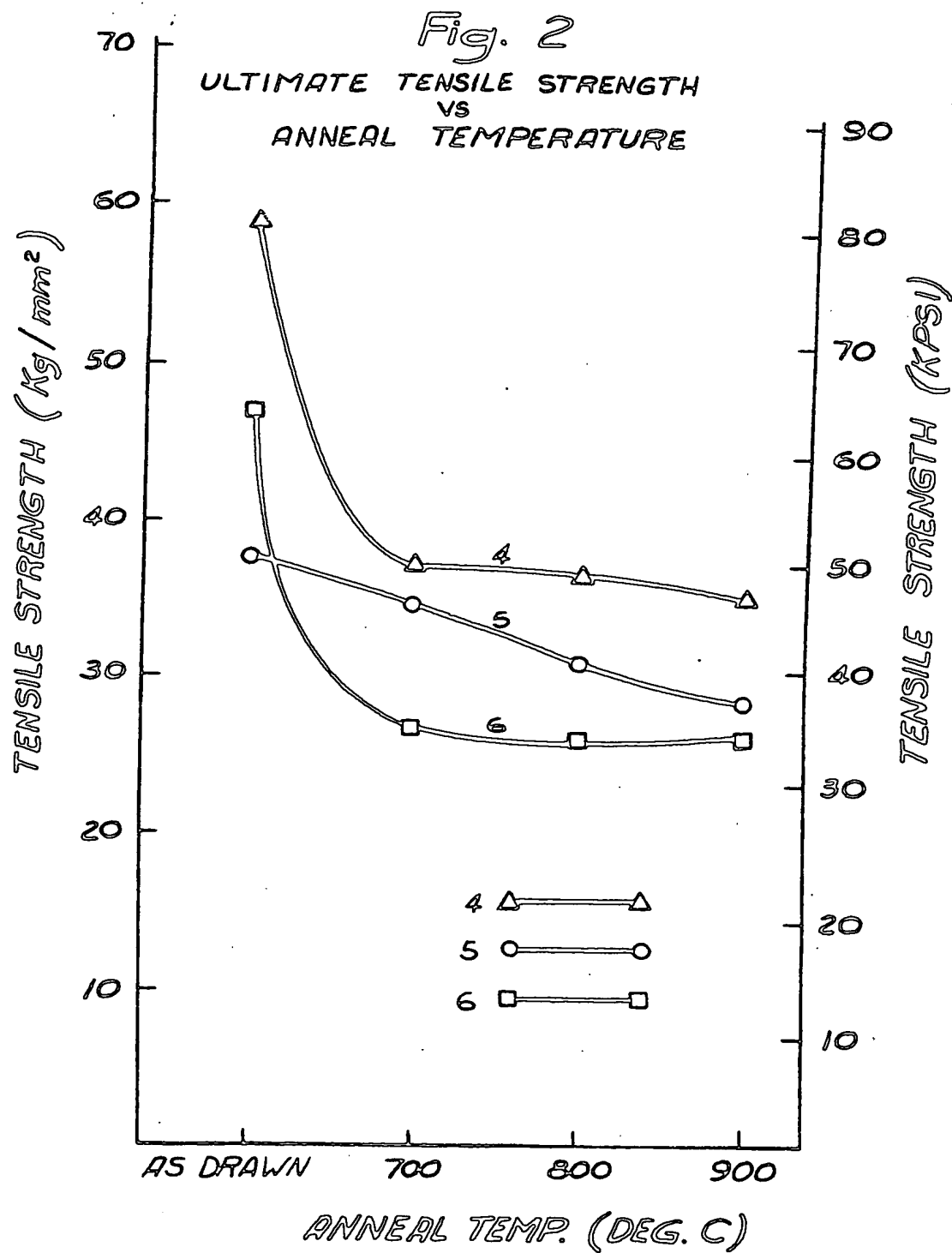
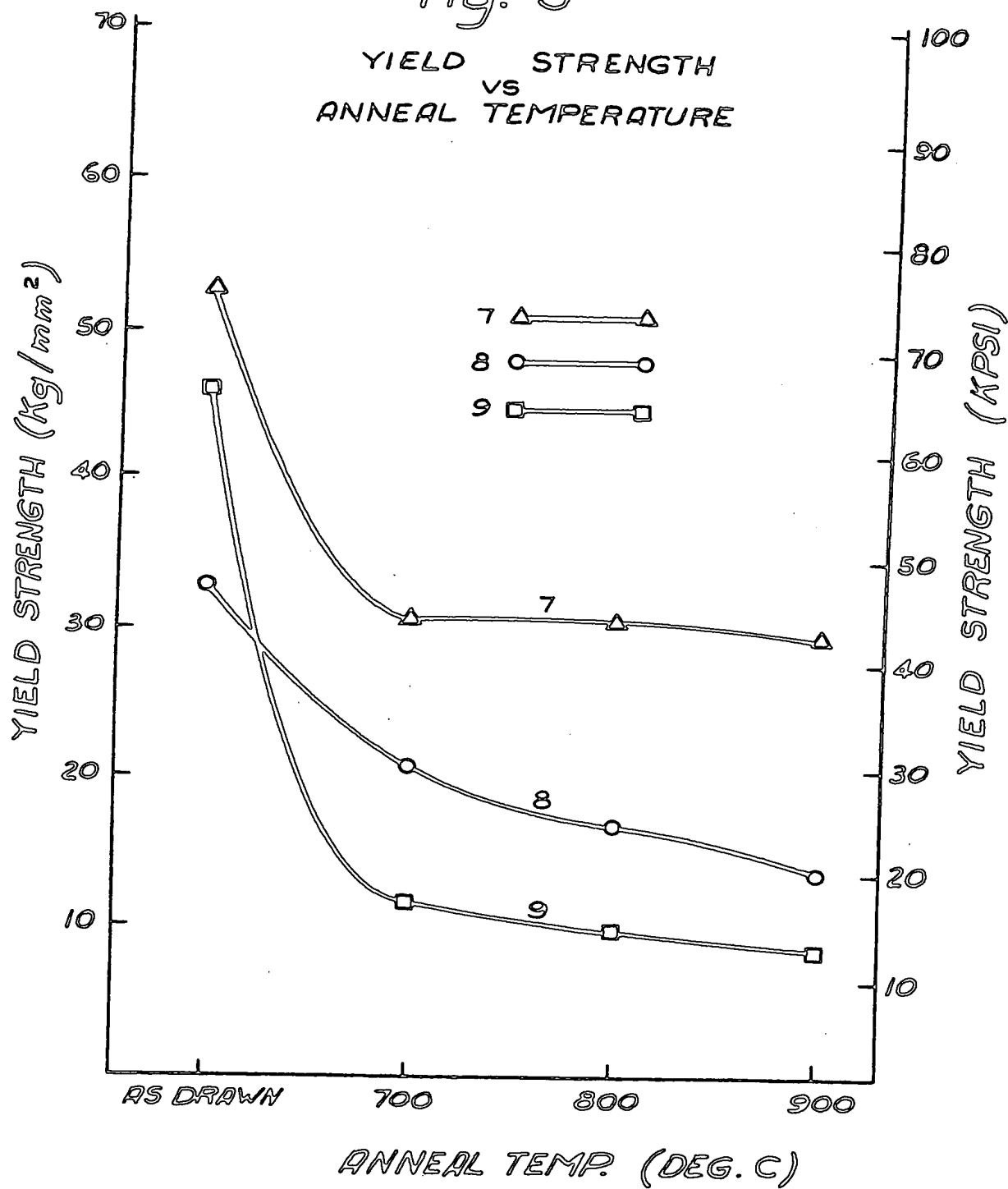


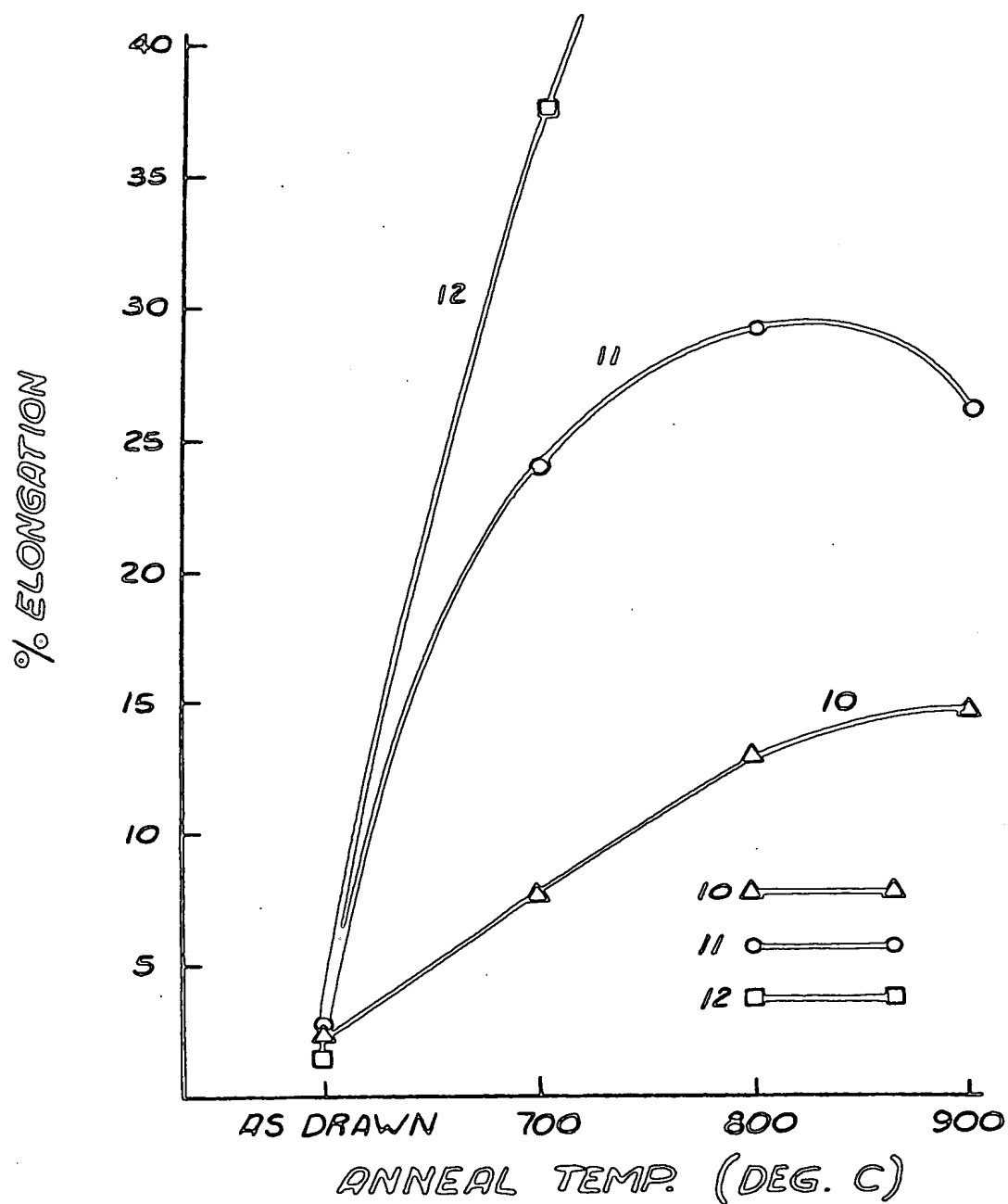
Fig. 3



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Fig. 4

% ELONGATION vs ANNEAL TEMPERATURE



## SPECIFICATION

## Dispersion-strengthened copper alloys

Sintered dispersion-strengthened copper alloys having aluminum oxide particles uniformly

- 5 dispersed therein are known and can be obtained from powder mixtures prepared by various techniques including mechanical mixing of the aluminum oxide with copper metal particles, internal oxidation, co-precipitation of aluminum
- 10 and copper compounds, simultaneous precipitation, and melting of the metal nitrate compounds. For example in British Pat. No. 917,005 there is disclosed a preparation method utilizing a copper powder mixture having
- 15 aluminum oxide dispersed throughout at least in part as a coating on the copper metal particles. The reported mechanical strength and ductility characteristics of the sintered products lacked sufficient improvement over other copper alloys,
- 20 however, to result in any widespread commercial acceptance of this material. The internal oxidation method of preparation has achieved commercial success since very fine dispersoids can be produced in the final sintered alloy in this manner
- 25 for improved mechanical properties and the concentration of the dispersoid can be controlled quite carefully. On the other hand, said commercially preferred method of preparation is also accompanied by various disadvantages
- 30 including difficulty of controlling dispersoid particle size and oxidation of the matrix metal at grain boundaries which reduces the mechanical strength of the dispersion strengthened alloy. Furthermore, the internal oxidation process is
- 35 limited by the diffusion rate of oxygen in the matrix metal which limits use of the sintered material to sheets, wire or powder form.

- Internally oxidized type copper alloys dispersion strengthened with aluminum oxide are now being
- 40 sold as powdered mixtures for sintering to produce the final product shape desired. The commercial method of preparing such powder mixture of the copper metal particles and dispersion strengthening oxide starts with a copper-
- 45 aluminum solution alloy which is internally oxidized and part of this starting material remains in the powder product. Presence of residual solution alloy can cause undesired variation in the physical and metallurgical properties of the
- 50 sintered product, hence can represent a shortcoming for the alloy material prepared in this manner. The average particle size in the commercial powder mixture is also maintained around ASTM (E-112) Grain Size No. 6 which has
- 55 not always been found to produce optimum physical characteristics in the final sintered product. On the other hand, since the dispersed aluminum oxide phase resides within the individual copper alloy particles of said powder
- 60 mixture it is not difficult to maintain close proximity between the aluminum oxide particulates in order to enhance the dispersion strengthening characteristics.

Accordingly, it would be desirable to form a

- 65 sintered copper alloy product dispersion strengthened with aluminum oxide in an improved manner not as subject to the foregoing noted difficulties and which can also be carried out by a more direct and less costly preparation process
- 70 than internal oxidation. It would further be desirable to provide a sintered copper alloy product that is essentially free of solution alloy byproducts.

- Dispersion-strengthened copper alloy products
- 75 comprising a sintered matrix of copper metal particles having uniformly dispersed therein smaller size particles of aluminum oxide are prepared in accordance with the present invention exhibiting mechanical properties of tensile
- 80 strength, yield strength, hardness, and ductility intermediate between copper-chromium alloys and internally oxidized type copper alloys dispersion strengthened with aluminum oxide and which further excludes any significant solution
- 85 alloy content. By "solution alloy content" as used herein is meant a solution alloy of copper and aluminum metal. The terms "sintered and sintering" as used herein means partial or complete welding together or coalescence of the
- 90 powder particles and generally resulting from some combination of subjecting the powder mixture to pressure above atmospheric pressure at elevated temperatures below the melting
- 95 temperature of copper metal to produce densification of said powder mixture up to the theoretical density. A method of preparation is employed which forms a copper metal powder mixture containing smaller size particles of
- 100 aluminum oxide as a coating on the individual copper particles sufficient to prevent physical contact between said copper particles and which can be sintered in conventional fashion when heated to about 1050°C in a reducing
- 105 atmosphere to a density in the approximate range 6—8.9 grams/cubic centimeter forming the dispersion strengthened sintered alloy product. Said copper powder mixture is also prepared in a particular manner from a liquid slurry of the
- 110 copper metal particles in a liquid solution of a dissolved aluminum compound. This slurry is heated with sufficient mechanical agitation to maintain copper metal particles in suspension until all of the solvent has been removed and a dry
- 115 coating of amorphous alumina gel has been uniformly deposited upon the surface of the copper metal particles. Said dry coating is thereafter converted to crystalline alumina by heating the mixture at elevated temperatures of around 200°C or greater in a reducing
- 120 atmosphere.

- The copper metal particle size in the present powder admixtures is preferably maintained no greater than approximately 44 microns diameter in order to enhance the dispersion strengthening characteristics. As previously indicated, the
- 125 dispersion strengthening depends to some degree upon the spacing distance between the aluminum oxide particulates in the dispersed phase. For the present physical admixtures wherein the dispersed

aluminum oxide particulates reside only at the grain boundaries of the copper metal particles, the size of said copper metal particles establishes this spacing distance. Conventional sintering of the present powder admixtures also does not appreciably alter the spacing distance between the aluminum oxide particulates established in this manner. A relatively uniform coating of the individual copper metal particles with said aluminum oxide particulates effectively precludes direct sintering between uncoated copper metal particles which further helps achieve uniform physical characteristics in the sintered product when subjected to the same sintering conditions. For example, relatively uniform density values were reproduced in the density range above indicated when the present powder mixtures were pressed into compacts and sintered at approximately 1050°C, said density values only further varying with aluminum oxide content and sintering time period.

The presently improved dispersion strengthened sintered products are particularly suitable as the inlead material for electric lamps where mechanical strength and electrical conduction at elevated temperatures are important operational characteristics. For example, there is disclosed in recently issued U.S. Pat. Nos. 4,138,623 and 4,208,603, both assigned to the present assignee, use of copper alloys dispersion strengthened with alumina as inleads for incandescent and other type electric lamps and wherein the improved inleads generally support the refractory metal lamp filament. Said prior art metal inlead constructions can further include an outer metal sheath of the copper metal which is attributable to the manner by which said wire products have been manufactured. The sheath metal results from sealing the copper alloy powder in a copper metal container for conventional swaging or cold working to form the final wire product. Since the sintering action needed to produce the final copper alloy product can be carried out by various known power metallurgy techniques which do not require sealing the alloy powder in a container, however, the present improvement is understandably intended to encompass products having the above defined physical and metallurgical characteristics irrespective of preparation method.

In one preferred embodiment, the dispersion strengthened copper alloy of the present invention contains from approximately 0.1 weight percent up to approximately 1.2 weight percent aluminum oxide. The density after sintering of a different preferred dispersion-strengthened copper alloy product of the present invention is greater than the density of commercial internally oxidized type copper alloy having the same alumina content and given the same sintering treatment. Still a different preferred dispersion-strengthened copper alloy product according to the present invention is prepared by partially sintering the powder mixture at elevated pressure and temperature to form a compact which is thereafter sealed in a metal

container for conventional wire drawing to produce a fully sintered wire product having an outer metal sheath.

The novel process by which a suitable copper alloy powder can be prepared for sintering to produce the above defined final alloy product comprises the following steps:

(a) preparing a liquid slurry of copper metal particles in a liquid solution containing a dissolved aluminum compound,

(b) heating the slurry with sufficient mechanical agitation to maintain the copper metal particles in suspension until the solvent has been removed,

(c) containing the heating until a dry coating of amorphous alumina gel has been deposited upon the surface of the copper metal particles, and

(d) converting the dry coating into crystalline alumina by heating the product at elevated temperatures of at least 200°C in a reducing atmosphere.

In carrying out the above process, an aqueous slurry of the suspended copper particles can be employed that includes a water soluble aluminum compound such as an organic or inorganic aluminum salt. The reducing atmosphere used in said process can be hydrogen or some other suitable reducing atmosphere which prevents oxidation of the copper particles when heated to elevated temperatures. It is also important during the above defined process to provide sufficient mechanical agitation of the liquid slurry to prevent formation of a supernatant liquid layer which can result in a non-uniform coating of the suspended particles with alumina gel and lead to undesired direct sintering between uncoated or non-uniformly coated particles.

The present invention will be further described, by way of example only, with reference to the accompanying drawings of which:—

FIG. 1 depicts variation in mechanical hardness of the present sintered copper alloy product at elevated temperatures;

FIG. 2 depicts the ultimate tensile strength of said alloy products after the same annealing treatment;

FIG. 3 is another graph depicting the yield strength of said alloy products after the same annealing treatment; and

FIG. 4 depicts ductility variation of the same annealed alloy products as measured by percent elongation.

In practicing the present invention, a suitable copper metal powder mixture is prepared coated uniformly with smaller size particles of aluminum oxide. Accordingly, approximately 81.7 grams of aluminum nitrate are dissolved in approximately 500 milliliters of distilled water and said solution then stirred into approximately 6 pounds of finely divided copper powder having an average particle size finer than 325 US Screen size. Said aqueous slurry is thereafter heated to approximately 95°C with continued mechanical agitation to maintain the copper metal particles suspended in the liquid medium until all water has been removed and without permitting formation of a supernatant

liquid layer in the liquid suspension during the water removal. Examination of the dry copper powder mixture observed that a uniform deposit of amorphous alumina gel coated the copper

- 5 particles and prevented physical contact therebetween. The dry powder mixture is thereafter further dried at approximately 100°C in air for approximately one hour and placed in a vacuum for an additional twelve hours. After said  
10 drying procedure, the powder mixture is thereafter ball milled with isopropyl alcohol for one hour and then dried again in air. The air dried mixture is then heated at approximately 800°C in hydrogen for about three hours which converts the amorphous  
15 aluminum oxide gel coating on the copper particles to a coating of crystalline aluminum oxide. Grinding of the converted powder mixture followed by passage through a 250 micron opening screen produces a powder suitable for  
20 sintering in a conventional manner.

- For example, the above prepared copper alloy powder mixture was sintered at approximately 1050°C in hydrogen after conventional hydropress compaction at approximately  
25 28,000 psi. A density of approximately 6.71 grams per cubic centimeter was obtained after four hours sintering which increased to approximately 6.80 grams per cubic centimeter after twelve hours sintering at the same heating  
30 conditions but did not increase significantly in density with prolonged further sintering. A density range of approximately 6.0—8.9 grams per cubic centimeter was obtained at the same sintering conditions for other copper alloy powders  
35 prepared in the same general manner above generally described but which include various alumina contents in the range from approximately 0.1 weight percent up to approximately 1.2 weight percent aluminum oxide. A commercially  
40 available internally oxidized copper powder mixture containing approximately the same weight percent alumina content as the above specifically illustrated embodiment was also sintered at the same sintering conditions and  
45 found to have a lower density of approximately 6.35 grams per cubic centimeter after four hours of sintering. Continuing sintering of said commercial copper powder mixture produced a density of approximately 6.48 grams per cubic  
50 centimeter after a twelve hour sintering time period thereby confirming the generally lower density obtained with the commercial powder. Additionally, it was observed that the copper metal particle size in the present sintered products  
55 are generally smaller than is obtained with commercial internally oxidized type copper alloy powders.

- Various physical properties were measured upon the present dispersion strengthened copper alloy product above illustrated for comparison  
60 with values obtained upon a commercial copper-chromium alloy containing approximately 1.0 weight percent chromium (designated CA182) as well as the commercial internally oxidized copper  
65 alloy product also above illustrated. Each of the

copper alloy products being compared were formed as wire samples having a diameter of approximately .014 inch using conventional processing techniques. Specifically, the respective

- 70 copper alloy mixture powders were first hydropressed to form a compact and thereafter sealed in a copper metal container for wire drawing, followed by hot extrusion of the copper clad billets, and finally drawing the billets into the  
75 desired wire products. The copper sheath material was removed by electrolytic etching of said wire products in a nitric acid and alcohol solution so as not to influence results obtained upon the respective copper alloys per se. The reported  
80 measurements were conducted at room temperature upon said prepared wire samples after annealing in argon for approximately 30 minutes at the reported elevated temperatures.

- Fig. 1 is a graph depicting the variation in room  
85 temperature hardness measurements made upon said above prepared wire products after annealing at the elevated temperatures reported in said graph. Conventional Vickers Diamond Pyramid Hardness (DPH) measurements were carried out  
90 upon the wire samples with a Tukon Microhardness tester using a 100 gram load and starting with the "as drawn" wire condition. Curve 3 represents the hardness values for wire samples of the commercial internally oxidized copper alloy  
95 product now being employed as the inlead material in incandescent lamps. While somewhat lower hardness values were obtained for the wire samples of the present copper alloy product as shown in Curve 2 said values are higher than  
100 reported in Curve 1 for the commercial copper-chromium alloy wire now being employed for inleads in said electric lamps.

- In Fig. 2 there is shown the variation in ultimate  
105 tensile strength for the same wire materials after the same annealing treatment above reported. Said measurements along with the hereinafter reported yield strength and percentage elongation measurements were conducted on an Instron tensile tester using a gage length of 1.0 inch at a crosshead speed of 0.20 inch per minute. Again, it  
110 can be noted in Fig. 2 that the ultimate tensile strength values reported upon said commercial internally oxidized copper alloy product in Curve 4 remained higher than reported in Curve 5 for the present copper alloy product. Still lower values are  
115 reported in Curve 6 for the commercial copper-chromium alloy wire samples. The ultimate tensile strength for the present copper alloy product is thereby intermediate between that for inlead materials now being used in said electric lamps.  
120 Correspondingly, the yield strength measurements reported in Fig. 3 and carried out with the same wire materials further confirmed the same intermediate relationship between the present  
125 copper alloy product and said commercial inlead materials. Curves 7 and 9 report the internally oxidized and copper-chromium alloy products, respectively, whereas Curve 8 is the yield strength variation with annealing temperature for the  
130 present copper alloy product. The percent



elongation measurements reported in Fig. 4 still further confirm the same interrelationship between said inlead materials. The Curve 10 values were obtained upon the same internally oxidized copper alloy product while the Curve 12 values represent the copper-chromium alloy product and Curve 11 located intermediate therebetween represents the present copper alloy product. As evident from said ductility measurements, the present copper alloys are more ductile than internally oxidized type materials which was not expected. It had been reported that limiting the presence of the aluminum oxide particles to the grain boundaries of the copper metal particles produced less ductility. Such ductility improvement understandably facilitates mechanical working of the present copper alloys.

It will be apparent from the foregoing description that a novel dispersion strengthened copper alloy material has been described which is generally useful especially for elevated temperature product applications. It should also be apparent from said description that modified compositions other than above specifically disclosed can be prepared in the same manner without sacrificing the disclosed desirable physical metallurgical characteristics. For example, while a copper sheath has been disclosed as useful in preparing the copper wire products of the present invention, it is further contemplated that still other metals can be used advantageously, such as nickel. Substitution of nickel in this manner could subsequently form a solution alloy with copper curing the wire drawing operation for possible further advantage in lamp inlead product applications. It is intended to limit the present invention, therefore only by the scope of the following claims.

#### CLAIMS

1. A dispersion-strengthened copper alloy comprising a sintered matrix of copper metal particles having uniformly dispersed therein smaller size particles of aluminum oxide which exhibits mechanical properties of tensile strength, yield strength, hardness and ductility intermediate between copper-chromium alloys and internally oxidized type copper alloys dispersion strengthened with aluminum oxide particles and which further excludes any significant solution alloy content.

2. A copper alloy as claimed in claim 1 containing from 0.1 weight percent up to 1.2 weight percent aluminum oxide.

3. A copper alloy as claimed in claim 1 or claim 2 wherein the density after sintering is

greater than the density of said internally oxidized type copper alloy having the same aluminum oxide content and given the same sintering treatment.

4. A copper alloy as claimed in any one of the preceding claims wherein the copper metal particle size is also smaller than for said internally oxidized type copper alloy.

5. A copper metal powder mixture containing smaller size particles of aluminum oxide as a coating on the individual copper particles sufficient to prevent physical contact between said copper particles and which can be sintered when heated to about 1050°C in a reducing atmosphere to a density in the range 6—8.9 grams/cc and form a dispersion strengthened copper metal alloy having uniformly dispersed therein smaller size particles of aluminum oxide.

6. A copper powder mixture as claimed in claim 5 containing from 0.1 weight percent up to 1.2 weight percent aluminum oxide.

7. A copper powder mixture as claimed in claim 5 or claim 6 which is further sealed in a metal container for wire drawing.

8. A process for preparing a copper powder mixture which can be sintered to form a dispersion-strengthened copper alloy having uniformly dispersed therein smaller size particles of aluminum oxide comprising:

(a) preparing a liquid slurry of copper metal particles in a liquid solution of a dissolved aluminum compound,

(b) heating the slurry with sufficient mechanical agitation to maintain the copper metal particles in suspension until the solvent has been removed,

(c) continuing the heating until a dry coating of amorphous alumina gel has been deposited upon the surface of the copper metal particles, and

(d) converting the dry coating to crystalline alumina by heating the product at elevated temperatures of at least 200°C in a reducing atmosphere.

9. A process as claimed in claim 8 wherein the liquid slurry is an aqueous slurry.

10. A process as claimed in claim 8 or claim 9 wherein the aluminum compound is an aluminum salt.

11. A process as claimed in any one of claims 8 to 10 wherein the reducing atmosphere is hydrogen.

12. A process as claimed in any one of claims 8 to 11 wherein the liquid slurry is heated under conditions preventing formation of a supernatant liquid layer.

13. A process as claimed in claim 8 substantially as hereinbefore described.

14. A copper alloy as claimed in claim 1 substantially as hereinbefore described.

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